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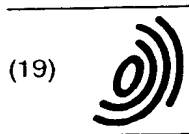
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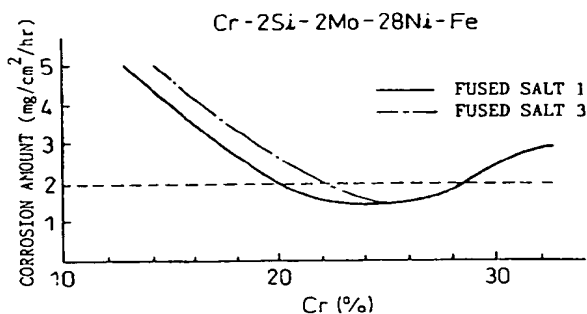
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(54) **ALLOY HAVING HIGH CORROSION RESISTANCE IN ENVIRONMENT OF HIGH CORROSIVENESS, STEEL PIPE OF THE SAME ALLOY AND METHOD OF MANUFACTURING THE SAME STEEL PIPE**

(57) The present invention provides a highly corrosion-resistant alloy used as a boiler tube in equipment the energy source of which is obtained by burning fossil fuel or waste, a steel tube for which the alloy is used, and a process for producing the steel tube. The alloy comprises up to 0.05% of C, 1.0 to 2.6% of Si, 0.02 to 1.0% of Mn, 20.0 to 28.0% of Cr, 18.0 to 30.0% of Ni, up to 4.0% of Mo, up to 0.05% of Al, 0.05 to 0.30% of N and the balance Fe and unavoidable impurities. Furthermore, the present invention also provides a multilayer steel tube having the alloy as a liner material and a standardized boiler tube as a base layer material, and a process for producing the multilayer steel tube.

Fig.1



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impurities, and satisfying the following formula:

$$(\text{Cr} + 2\text{Si} + 0.5\text{Mo}) > \text{Ni} \geq 1.1(\text{Cr} + 1.5\text{Si} + 0.5\text{Mo}) - 8, \text{ and}$$

$$\text{Mo}(\text{Cr} - 18) \geq 8$$

(2) The alloy according to item (1) excellent in corrosion resistance in an environment where fuel of poor quality and waste are burnt, wherein the alloy comprises 0.10 to 0.30% of N in terms of weight.

(3) The alloy according to item (1) or (2) excellent in corrosion resistance in an environment where fuel of poor quality and waste are burnt, wherein the alloy comprises, in terms of weight, 0.02 to 0.05% of C, 1.60 to 2.2% of Si, 23.0 to 27.0% of Cr, 23.0 to 27.0% of Ni and 2.0 to 4.0% of Mo.

(4) The alloy according to any one of item (1) to (3) excellent in corrosion resistance in an environment where fuel of poor quality and waste are burnt, wherein the alloy further comprises up to 0.4% of Nb.

(5) A steel tube excellent in corrosion resistance in an environment where fuel of poor quality and waste are burnt, the steel tube comprising the alloy according to any one of item (1) to (4).

(6) A multilayer steel tube excellent in corrosion resistance in an environment where fuel of poor quality and waste are burnt, the multilayer steel tube comprising a standardized boiler tube (JIS G3461, G3462, G3463) as a base layer material, and an alloy according to any one of item (1) to (4) as an outer layer material.

(7) A process for producing a steel tube excellent in corrosion resistance in an environment where fuel of poor quality and waste are burnt, comprising the steps of heating a billet of an alloy according to any one of item (1) to (4) to temperatures of 1,200 to 1,250°C, elongating the billet by hot extrusion, and cooling the elongated product to 550°C at a rate of at least 1°C/sec to form an austenite single phase structure.

Brief Description of the Drawings

Fig. 1 is a graph showing the influence of the amount of Cr on the corrosion amount in a fused scale simulation environment.

Fig. 2 is a graph showing the influence of the amount of Si on the corrosion amount in a fused scale simulation environment.

Fig. 3 is a graph showing the influence of the Ni content on the corrosion amount in a fused scale simulation environment.

Fig. 4 is a graph showing the influence of the Mo content on the corrosion amount in a fused scale simulation environment.

Fig. 5 is a graph showing the influence of the Ni content and the amount of $(1.1 \times (\text{Cr} + 1.5 \text{ Si} + 0.5 \text{ Mo}) - 8)$ on a flatten-close test.

Fig. 6 is a graph showing the relationship between the precipitation amount of the σ phase and the Si content under the conditions of respective processes.

Fig. 7 is a graph showing the relationship between a creep rupture time at 700°C under a load stress of 100 MPa and the N content.

Fig. 8 is a graph showing the effects of Cr and Mo on the inhibition of pitting corrosion in an environment where combustion products are being simulated.

Best Mode for Carrying Out the Invention

As the result of carrying out research on materials suited to a high temperature combustion environment where sulfates and chlorides such as Na_2SO_4 , NaCl , KCl and CaSO_4 are formed during combustion and adhere to and deposit on oxidized scales, the present inventors have made the discoveries described below.

(i) In the high temperature combustion environment, the corrosion resistance of the alloy does not depend on the Cr content alone but on a combination of Ni, Co and Mo. That is, an alloy having a high Cr content generally has a corrosion resistance in a high temperature oxidizing atmosphere environment having a high O_2 concentration. However, in power generation equipment which uses crude oil, heavy oil, tar, coal, and the like as fuel and in refuse incineration power generation equipment, the O_2 concentration is decreased for the purpose of decreasing NO_x . As a result, an alloy having a high Cr content does not necessarily have corrosion resistance.

(ii) In the high temperature combustion environment, since low melting point compounds such as an eutectic compound, for example, $\text{NaCl-Na}_2\text{SO}_4\text{-KCl-K}_2\text{SO}_4$ and NaCl-KCl-CaSO_4 are formed as scale on the alloy surface, fused scale is formed on the alloy surface. Consequently, scale on the alloy surface is locally fused, and protective scale disappears, which extraordinarily increases the corrosion rate. Moreover, hot erosion caused by fluid sand

It is understood from the results that those alloys in which the Cr, Si and Mo components are stipulated by the formulas mentioned above show a decreased amount of corrosion caused by a sulfate when the Ni content is at least 23.0% and less than 27.0% and thus show excellent corrosion resistance in fused salts having a slightly high concentration of a sulfate, whereas the alloys show an increased amount of corrosion caused by a sulfate when the Ni content is at least 27.0%.

Next, tests were conducted at 550°C in the same manner as the corrosion tests mentioned above, using Fused Salt 3 composed of 25% NaCl + 25% KCl + 25% Na₂SO₄ + 25% K₂SO₄ and corresponding to a waste incineration environment which contains about the same amounts of sulfates and chlorides. Figs. 1 and 2 show the test results with dotted lines.

Fig. 4 shows the influence of Mo on a corrosion amount, and alloys having chemical compositions composed of 25Cr-2Si-Mo-25Ni-Fe were used.

As a result of intensively performing investigations as described above, the present inventors have discovered that a steel having a Cr content of 20.0 to 28.0%, a Si content of 1.0 to 2.6%, a Ni content of 18.0 to 30.0% and a Mo content of up to 4.0% has high corrosion resistance in an environment where sulfates and chlorides coexist.

Furthermore, the present inventors have discovered that a steel having a Cr content of 23.0 to 27.0%, a Si content of 1.6 to 2.2%, a Ni content of 23.0 to 27.0% and a Mo content of 2.0 to 4.0% is more excellent in corrosion resistance, and that the steel has sufficiently high corrosion resistance in a waste incineration environment containing about the same amounts of sulfates and chlorides.

When the alloy of the present invention is used as a boiler tube, the alloy is required to inhibit deterioration of cold workability caused by precipitation of δ ferrite and the σ phase in addition to the corrosion resistance as mentioned above. Flatten-close tests in accordance with flatten tests specified by JIS G3463 were conducted to evaluate the cold workability of the alloy. Figs. 5 and 6 show the test results.

Fig. 5 is a graph showing the influence of a Ni content and an amount represented by the formula $(1.1(\text{Cr} + 1.5\text{Si} + 0.5\text{Mo}) - 8)$ on the results of flatten-close tests. When the alloy contains at least 20% of Cr and at least 1% of Si and has a high Mo content, δ -ferrite is formed to lower the cold workability. However, it has already been known that when $\text{Ni} \geq (\text{Cr} + 2\text{Si} + 0.5\text{Mo})$, cracks are not formed and high cold workability is obtained. Japanese Unexamined Patent Publication (Kokai) No. 7-243007 discloses the matter. The feature of the present invention is as follows: it has been discovered in the subsequent investigation that the alloy can maintain an austenitic structure, does not form cracks and shows high cold workability even when $(\text{Cr} + 2\text{Si} + 0.5\text{Mo}) > \text{Ni} \geq 1.1(\text{Cr} + 1.5\text{Si} + 0.5\text{Mo}) - 8$. Moreover, since the amount of Ni which is relatively costly can be decreased in the alloy of the present invention compared with alloys having already been applied, the cost of the alloy is low. Furthermore, the corrosion amount of the alloy of the invention can be suppressed particularly in an environment where the sulfate content is slightly high.

Fig. 6 is a graph showing the relationship between a precipitation amount of the σ phase and a Si content under the conditions of respective production processes. Alloys having chemical components composed of 24Cr-Si-2Mo-26Ni-Fe were used. The conditions (three conditions) of the production processes were as follows: Process 1: a heating temperature of 1,220°C and an average rate of cooling to 550°C of 1.3°C/sec; Process 2: a heating temperature of 1,180°C and an average rate of cooling to 550°C of 1.3°C/sec; and Process 3: a heating temperature of 1,220°C and an average rate of cooling to 550°C of 0.8°C/sec. In addition, cracks were formed during hot extrusion in Process 2. It is seen from Fig. 6 that in the production of a single layer tube by a hot extrusion process, the desirable Si content is up to 2.2%.

When the alloy of the present invention is used as a boiler tube, the tube is naturally required to have a high temperature strength to a certain degree because the tube is a pressure-resistant member. Addition of N is effective in inhibiting the precipitation of the σ phase which causes a drastic strength decrease during use at high temperature.

Fig. 7 is a graph showing the relationship between a creep rupture time at 700°C under a load stress of 100 MPa and a N content. Alloys having chemical constituents composed of 25Cr-2Si-3Mo-25Ni-Fe-N were used. It is understood from Fig. 7 that the optimum N content is from 0.05 to 0.3%, or that from the standpoint of inhibiting the σ phase the optimum one is from 0.1 to 0.3%.

The alloy of the present invention must have resistance to corrosion and pitting corrosion taking place as a result of presence of chlorides in combustion products and an oxidizing environment at the time of stopping combustion of a boiler, etc. Composite addition of Cr and Mo is effective in inhibiting the pitting corrosion. To examine the effects, pitting corrosion tests were conducted in a solution containing 5% of FeCl₃ simulating a combustion product. Fig. 8 shows the test results.

Fig. 8 is a graph showing the effects of Cr and Mo on the inhibition of pitting corrosion formation. The corrosion tests were conducted at 40°C in a solution containing 5% of FeCl₃. When the Cr content is from 20.0 to 28.0%, the following conditions must be satisfied to inhibit the pitting corrosion formation: an addition amount of Mo of up to 4%, and $\text{Mo}(\text{Cr} - 18) \geq 8$.

From the results as described above, the range of the chemical constituents of the alloy of the present invention are defined as follows.

amount enough to inhibit the formation of Cr carbides. Since the weight ratio of Nb to C is approximately 8 in the Nb carbide, to obtain excellent corrosion resistance even after the addition of Nb, the addition amount of Nb must be restricted to up to 0.4%, and the Nb content must satisfy the following formula:

$$\text{Nb} \geq 8\text{C}$$

Al: Al is added as a deoxidizer during the production of the alloy. Since the addition of Al in a large amount embrittles the alloy of the present invention when the alloy is used at high temperature over a long period of time, the addition amount is restricted to up to 0.05%.

N: N is an effective, low cost austenite-stabilizing element. N improves the high temperature strength of the alloy necessary for a boiler tube, and has an effect of inhibiting the precipitation of the σ phase which becomes a cause of a decrease in the strength of the alloy when the alloy is used for a long time.

As shown in Fig. 7, N shows the effect of improving the high temperature strength when N is added in an amount of at least 0.05%. Moreover, addition of N in an amount of at least 0.1% is desirable from the standpoint of inhibiting the σ phase. Excessive addition of N results in precipitation of nitrides in a large amount, which cause extraordinary corrosion. The addition amount is, therefore, restricted to up to 0.3%.

Next, the process for producing a steel tube from the alloy of the present invention will be explained.

A billet of the alloy of the present invention is produced by the conventional melting-casting process of a stainless steel. The billet is used as a material for hot extrusion in an as forged or as cast state. When a single layer tube is to be produced from the alloy to which the addition amount of Si is large, the σ phase may have been precipitated during solidifying the billet or cooling subsequently to forging. Since the σ phase causes crack formation during elongation by hot extrusion, the billet is heated at temperatures of at least 1,200°C for at least 30 minutes to make the σ phase disappear sufficiently, and immediately hot extruded to prevent reprecipitation. The upper limit of the billet heating temperature is restricted to be 1,250°C to prevent fused embrittlement. The σ phase may precipitate in the cooling step directly after hot extrusion, and cause crack formation when cold drawing is conducted in the next step. Moreover, the σ phase may also cause crack formation during bending even when the as hot extruded product is used. To prevent the precipitation of the σ phase, the hot extruded product is cooled at an average cooling rate of at least 1°C/sec until the temperature reaches 550°C to form an austenite single phase structure.

The production conditions are based on the results in Fig. 6. That is, Fig. 6 shows the results of investigating the relationship between a Si content and a precipitation amount of the σ phase, for billets produced by the following three processes: Process 1: a billet heating temperature of 1,220°C and an average rate of cooling to 550°C of 1.3°C/sec; Process 2: a billet heating temperature of 1,180°C and an average rate of cooling to 550°C of 1.3°C/sec; and Process 3: a billet heating temperature of 1,220°C and an average rate of cooling to 550°C of 0.8°C/sec. In Process 1, when the billet had a Si content of up to 2.2%, the σ phase did not precipitate, and cracks were not formed. In Process 2, hot extrusion was conducted while the σ phase did not disappear sufficiently due to a low heating temperature of the billet, and consequently cracks were formed during hot extrusion. In Process 3, since the cooling rate was slow, the σ phase precipitated during cooling even when the Si content was about 1.0. In the present invention, any known procedure can be applied in the cooling step at temperatures of less than 550°C and in the working step subsequently to hot extrusion. Needless to say, the production process of the present invention is not restricted to the single layer tube but it can be applied to the production of a multilayer tube.

Next, the process for producing a multilayer steel tube of the present invention will be explained.

Powder of the alloy of the present invention for an outer tube is press bonded by hydraulic isostatic pressing (HIP) to the surface of a given stainless steel billet for an inner tube produced by a conventional melting-casting process of the stainless steel. The billet for a double layer tube is soaked, and hot extruded to have a given size.

When the material for the outer tube is a plate or tube, in place of the process for press bonding the powder by HIP, the plate having chemical constituents of the outer tube material is wound around the stainless steel billet for the inner tube, or the stainless steel billet is fitted into the outer tube material. The outer tube material and the inner tube material are then bonded by welding, and a multilayer steel tube is produced using the billet for a double tube thus produced by the process as mentioned above. When the alloy of the present invention has a high Si content, the alloy shows lowered hot deformability when subjected to conventional hot working. However, the alloy shows no lowered hot deformability during tubing when hot extrusion by HIP is employed.

When the alloy of the present invention is used for the multilayer steel tube, a carbon steel, a low alloy steel or stainless steel specified by JIS G3461, JIS G3462, JIS G3463, etc., and used as a boiler tube is employed as a base layer material, and the alloy of the present invention is used as a liner material for the inner or outer layer to form a multilayer steel tube.

Needless to say, the process for producing the multilayer steel tube of the present invention is not limited to the production process as mentioned above, but other known processes for producing a composite or multilayer steel tube may also be adopted.

Table 1-1

No.	Category	Chemical composition (wt.%)								
		C	Si	Mn	Cr	Ni	Mo	Nb	Al	N
1	Alloy of I.	0.026	1.23	0.17	27.4	26.3	1.2	0.32	0.009	-
2	Alloy of I.	0.007	1.65	0.18	26.5	28.9	2.2	0.1	0.043	-
3	Alloy of I.	0.04	1.82	0.17	25.1	24.9	3.1	0.35	0.011	-
4	Alloy of I.	0.025	1.36	0.19	20.3	22.3	3.5	0.21	0.007	-
5	Alloy of I.	0.032	2.22	0.15	21.6	26.5	3.6	0.3	0.032	-
6	Alloy of I.	0.008	2.22	0.22	21.4	23.5	2.4	-	0.034	-
7	Alloy of I.	0.031	2.22	0.31	27.3	29.1	1.5	-	0.023	-
8	Alloy of I.	0.029	1.25	0.92	20.2	18.8	3.7	-	0.012	-
9	Alloy of I.	0.009	1.81	0.75	21.6	26.5	3.6	0.28	0.032	-
10	Alloy of I.	0.031	1.74	0.21	25.1	25.1	3.1	0.3	0.01	0.18
11	Alloy of I.	0.029	1.76	0.34	25	25.8	2.9	0.28	0.01	0.06

Table 1-1 (Continued)

No.	Category	Corrosion test (mg/cm ² /hr)				Flattening close test
		Fused Salt 1*	Fused Salt 2#	Fused Salt 3*	Pitting corrosion	
1	Alloy of I.	1.7	1.9	2.6	Not formed	No crack
2	Alloy of I.	1.6	2.1	2.2	Not formed	No crack
3	Alloy of I.	1.7	1.8	1.9	Not formed	No crack
4	Alloy of I.	1.9	2.3	2.4	Not formed	No crack
5	Alloy of I.	1.8	2.1	1.8	Not formed	No crack
6	Alloy of I.	1.9	2	1.8	Not formed	No crack
7	Alloy of I.	1.7	2.1	1.7	Not formed	No crack
8	Alloy of I.	1.9	1.9	2.7	Not formed	No crack
9	Alloy of I.	1.8	2.2	1.9	Not formed	No crack
10	Alloy of I.	1.7	1.8	2	Not formed	No crack
11	Alloy of I.	1.6	2	1.9	Not formed	No crack

Note: Alloy of I. = Alloy of Invention

*Fused Salt 1: 15% NaCl + 15% KCl + 5% CaSO₄ + 65% PbCl₂

#Fused Salt 2: 55% CaCl₂ + 20% NaCl + 5% KCl + 20% MgSO₄

*Fused Salt 3: 25% NaCl + 25% KCl + 25% Na₂SO₄ + 25% K₂SO₄

Table 2

No.	Process of Invention		Comparative Process 1		Comparative Process 2	
	during hot extrusion	flattening close test	during hot extrusion	flattening close test	during hot extrusion	flattening close test
17	No crack	No crack	Crack formed	Crack formed	No crack	Crack formed
18	No crack	No crack	Crack formed	Crack formed	No crack	Crack formed
19	No crack	No crack	Crack formed	Crack formed	No crack	Crack formed
20	No crack	No crack	Crack formed	Crack formed	No crack	Crack formed
21	No crack	No crack	Crack formed	Crack formed	No crack	Crack formed
22	No crack	No crack	Crack formed	Crack formed	No crack	Crack formed
23	No crack	No crack	Crack formed	Crack formed	No crack	Crack formed
24	No crack	No crack	Crack formed	Crack formed	No crack	Crack formed
25	No crack	No crack	Crack formed	Crack formed	No crack	Crack formed
26	No crack	No crack	Crack formed	Crack formed	No crack	Crack formed
Note: Process of Invention: a billet heating temperature of 1,220°C, an average rate of cooling to 550°C of 1.3°C/sec Comparative Process 1: a billet heating temperature of 1,180°C, an average rate of cooling to 550°C of 1.3°C/sec Comparative Process 2: a billet heating temperature of 1,220°C, an average rate of cooling to 550°C of 0.8°C/sec						

The present invention provides an alloy, a single layer tube and a multilayer tube having excellent corrosion resistance in an environment where fuel of poor quality such as one containing Na, K, S and Cl, and waste such as industrial waste, municipal refuse and sewage sludge are burnt. As a result, the present invention has made it possible to provide a furnace wall tube, a steam superheater tube, and the like having high corrosion resistance in the environment mentioned above.

Claims

1. An alloy having excellent corrosion resistance in an environment where fuel of poor quality and waste are burnt, the alloy comprising, in terms of weight, up to 0.05% of C, 1.0 to 2.6% of Si, 0.02 to 1.0% of Mn, 20.0 to 28.0% of Cr, 18.0 to 30.0% of Ni, up to 4.0% of Mo, up to 0.05% of Al, 0.05 to 0.30% of N and the balance Fe and unavoidable impurities, and satisfying the following formulas:

$$(Cr + 2Si + 0.5Mo) > Ni \geq 1.1(Cr + 1.5Si + 0.5Mo) - 8, \text{ and}$$

$$Mo(Cr - 18) \geq 8$$

2. The alloy according to claim 1 excellent in corrosion resistance in an environment where fuel of poor quality and waste are burnt, wherein the alloy comprises 0.10 to 0.30% of N in terms of weight.
3. The alloy according to claim 1 or 2 excellent in corrosion resistance in an environment where fuel of poor quality and waste are burnt, wherein the alloy comprises, in terms of weight, 0.02 to 0.05% of C, 1.60 to 2.2% of Si, 23.0 to 27.0% of Cr, 23.0 to 27.0% of Ni and 2.0 to 4.0% of Mo.
4. The alloy according to any one of claims 1 to 3 excellent in corrosion resistance in an environment where fuel of poor quality and waste are burnt, wherein the alloy further comprises up to 0.4% of Nb.
5. A steel tube excellent in corrosion resistance in an environment where fuel of poor quality and waste are burnt, the steel tube comprising the alloy according to any one of claims 1 to 4.
6. A multilayer steel tube excellent in corrosion resistance in an environment where fuel of poor quality and waste are

Fig.1

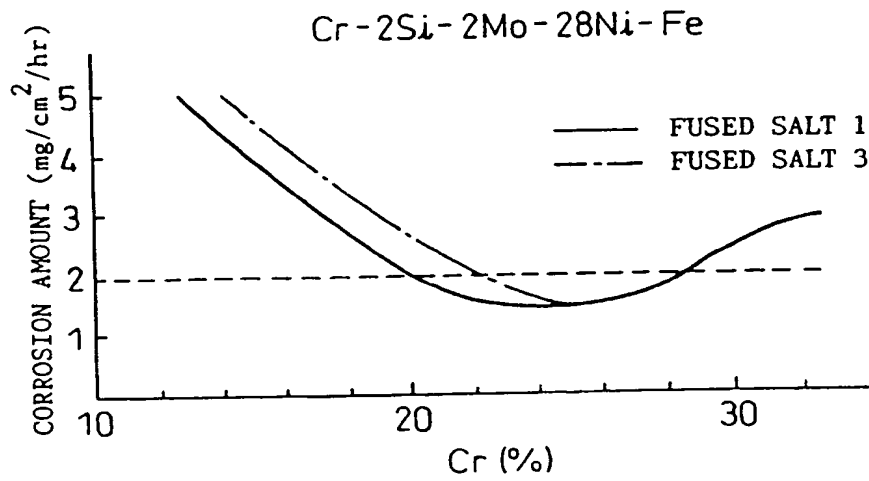


Fig.2

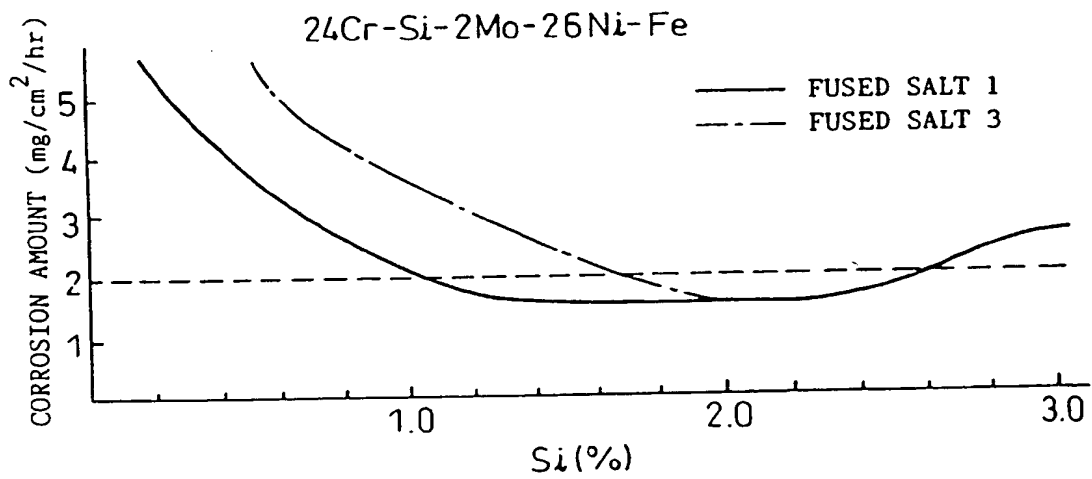


Fig.5

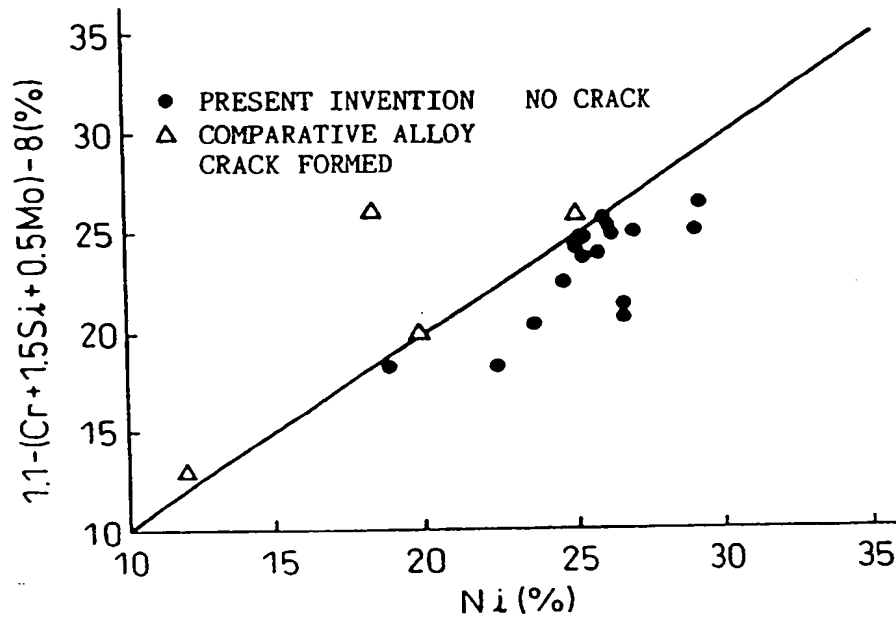
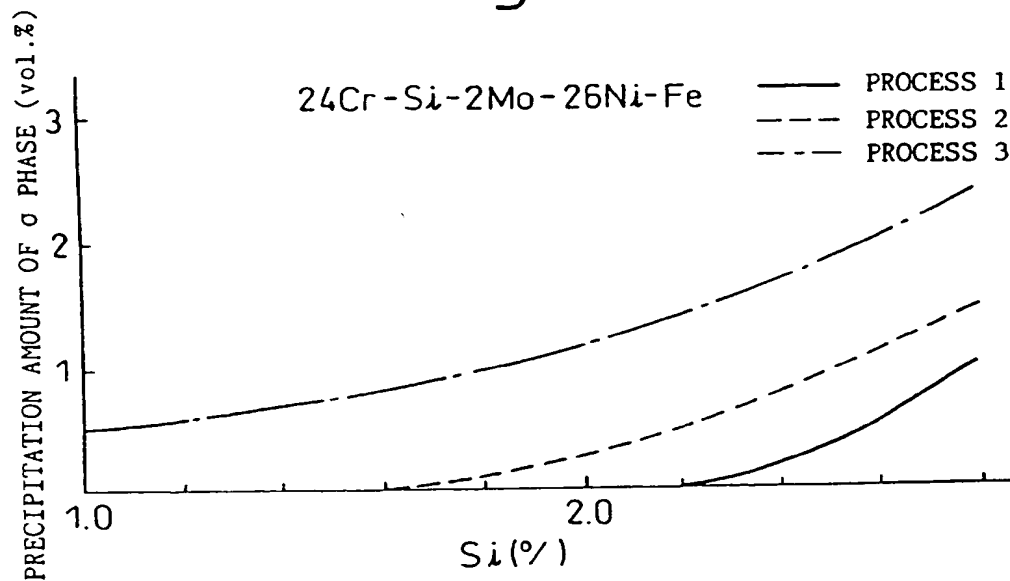


Fig.6



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP97/01302

A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl⁶ C21D8/10, C22C38/00, B32B1/08

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Int. Cl⁶ C21D8/00-10, C22C38/00-60, B32B1/08

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

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Kokai Jitsuyo Shinan Koho	1971 - 1997	Koho
Toroku Jitsuyo Shinan Koho	1994 - 1997	1996 - 1997

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP, 4-350149, A (Sumitomo Metal Industries, Ltd.), December 4, 1992 (04. 12. 92) & US, 5378427, A	1 - 7
A	JP, 7-243007, A (Nippon Steel Corp.), September 19, 1995 (19. 09. 95) & EP, 709479, A1 & US, 5620805, A & WO, 9524512, A1	1 - 7

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Date of the actual completion of the international search

June 4, 1997 (04. 06. 97)

Date of mailing of the international search report

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